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RESEARCH MEMORANDUM

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SUMMARY OF THE AVAILABILITY AND PERFORMANCE

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PROBLEMS OF HIGH OCTANE NUMBER FUELS

By authority of

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NACA Subcommittee on Aircraft Fuels

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

WASHINGTON

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

SUMMARY OF THE AVAILABILITY AND PERFORMANCE

PROBLEMS OF HIGH OCTANE NUMBER FUELS

By

NACA Subcommittee on Aircraft Fuels

SUMMARY

A study has been conducted by the NACA Subcommittee on Aircraft Fuels of the NACA Committee on Power Plants to determine the possible blending agents or additives that may be used to supplement current high performance number, rich rating components in future aviation fuels. These compounds have been surveyed with a view to their application in Grades 100/130 and 115/145 aviation fuels containing 4.6 ml TEL per gallon and in aviation fuels containing only 3.0 ml TEL per gallon but meeting the same rich performance rating.

This study of the availability of high octane number fuels in relation to their performance appears to indicate that such high rich rating blending agents as toluene and xylene cannot be made available in sufficient quantities to maintain the rich rating performance of the fuels when reducing the lead content from 4.6 to 3.0 ml per gallon. These aromatic blending components could, however, be produced in sufficient incremental quantities to overcome the possible lack in availability of cumene.

This study has also indicated that the requirements for ethers are about the same as for toluene and xylene as components to improve rich mixture performance. Certain ethers gave an even better knock-limited performance than aviation alkylate. Because of the lack of service experience and lack of well-developed production facilities a complete evaluation of ethers cannot be made at this time.

It would appear that aromatic amines could be made available in sufficient quantities to maintain rich mixture performance characteristics at the 3.0 ml per gallon lead level without significantly affecting availability. However, a rather extensive engine test program must be undertaken to establish performance of amine-containing blends in the most advanced engines under various types of operations before the aromatic amines can be counted upon in any long-range program.

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INTRODUCTION

The NACA Subcommittee on Aircraft Fuels of the NACA Committee on Power Plants has been informed that the utility of some of the newer long-range United States Air Force aircraft has been limited due to lead fouling of spark plugs and valves. Although this subcommittee has previously advised Military Services that relief from the lead fouling problem could be attained through the use of improved models of spark plugs now available or under development, use of improved lead scavengers and through better control of engine temperatures, the possibility of using lower lead content fuels should not be overlooked. It was, however, the expressed desire of the Services to maintain the rich mixture rating of the fuel. This would require the use of additional quantities of components with high rich mixture ratings. The Subcommittee, therefore, undertook to survey the possible supplementary sources of high performance number, rich rating components for aviation gasolines which would meet currently specified rich performance numbers (F-4) of 130 and 145 but would contain only 3.0 ml TEL per gallon. These supplementary materials include aromatics, ethers, and aromatic amines.

The problem of supplying a sufficient quantity of high performance number, rich rating components has been recently intensified by a review of chemical requirements for benzene under emergency conditions prepared by the National Security Resources Board. This survey would indicate that no benzene will be available for the manufacture of cumene for aviation gasoline blending. The subcommittee has surveyed the available information on aromatics, ethers and aromatic amines to determine possible blending agents or additives that might be substituted for cumene in future aviation fuels. It is the purpose of this report to present the results of this survey.

This review of the available information on cumene substitutes should not be construed as a recommendation by the subcommittee that the lead fouling problem can most easily be resolved by lowering the lead content of aviation fuels. The information contained herein does, however, indicate the cost and problems involved in lowering the lead content so that a more accurate comparison can be made between this method and other methods of alleviating the lead fouling problem.

The members of the Subcommittee on Aircraft Fuels when this study was made were:

Mr. W. M. Holaday, Chairman

Mr. E. C. Phillips

Commander R. J. Hoyle, USN

Mr. Donald B. Brooks

Mr. Kenneth S. Cullom

Dr. L. C. Gibbons

Mr. Floyd G. Dougherty

Dr. D. P. Barnard

Mr. A. J. Blackwood

Mr. S. D. Heron

Dr. J. Bennett Hill

Mr. C. R. Johnson

Dr. W. E. Kuhn

Mr. T. L. Anjohn, Professor G. G. Lamb, and Mr. Henry C. Barnett have been of considerable assistance to the subcommittee in its preparation of this report.

DISCUSSION OF RESULTS

Reference will be made in subsequent paragraphs to the "present plan" and the "alternate plan." "Present plan" refers to the production of either Grade 115/145 or Grade 100/130, or both, containing 4.6 ml TEL per gallon. "Alternate plan" refers to the production of a Grade 145 or Grade 130, or both, containing only 3.0 ml TEL per gallon. In the "alternate plan," only the rich mixture performance (F-4) number is specified, the lean mixture (F-3) performance number generally being somewhat lower than 115 and 100 in the Grades 145 and 130, respectively.

Availability of and Requirements for Rich Mixture Blending Agents. The report of the Military Petroleum Advisory Board Aircraft Fuels Committee, entitled "Summary Report on the Potential Production of High Antiknock Aviation Fuels," predicates potential production on the basis of the availability of 7500 barrels per day of benzene to produce 10,000 barrels per day of cumene. The report points out that this quantity of high rich rating blending stock must be made available if optimum production rates are to be attained from presently installed facilities. Production capacity is adversely affected regardless of whether all Grade 115/145 or Grade 100/130 or some intermediate quantities of each are produced.

A recent review of chemical requirements for benzene under emergency conditions, prepared by the National Security Resources Board, would indicate that no benzene will be available for the manufacture of cumene for aviation gasoline blending. This situation makes more difficult the problem of maintaining a high rich mixture antiknock quality level when reducing the lead content from 4.6 to 3.0 ml per gallon. It has been established that under these conditions approximately 32,000 barrels per day of cumene using 24,000 barrels per day of benzene would be required to maintain the rich rating levels and, at the same time, maximum availability of Grades 130 and 145. This is obviously impossible in the light of benzene supplies. Other sources of high quality rich mixture blending agents must then be investigated.

Appendix A of this report summarizes most of the information available on the aromatics and ethers which in the past have been investigated as possible blending agents for aviation gasoline. No aromatic hydrocarbons boiling in a range higher than cumene can be considered suitable substitutes because of fuel volatility specification limitations. With the use of benzene automatically eliminated because of limited availability and the high cost in terms of both investment and steel requirements to supplement the supply from petroleum sources, only ethyl benzene, m-xylene, p-xylene and toluene remain.

It would appear that ethyl benzene, per se, could be immediately eliminated. During the last war and during any emergency in the near future, requirements for ethyl benzene would be fulfilled by the alkylation of benzene with ethylene. Ethyl benzene is present in certain petroleum fractions; however, any recovery therefrom would be secondary to the recovery of m-xylene and p-xylene which would be accomplished simultaneously.

Toluene requirements equivalent to cumene under the present and alternate programs (maintaining rich ratings of 130 and 145 at 4.6 and 3.0 ml TEL per gallon, respectively) are 11,000 and 35,000 barrels per day, respectively. Raw stocks for the manufacture of the lower quantity could undoubtedly be made available and requirements met by the installation of hydroformer and extraction equipment at rather high cost in terms of dollars and metal requirements. The possibility of producing the larger quantity is highly questionable and would require a careful study of charge stock availability and other factors.

Xylene requirements equivalent to the cumene under the present and alternate programs are approximately 10,500 and 34,000 barrels per day, respectively. This material could be extracted together with toluene from catalytically cracked stocks to the extent that they were not required for direct blending (as high quality base stocks) in the 130 and 145 Grades. Here again, presently programmed requirements could undoubtedly be met (using 4.6 ml TEL per gallon). Meeting the alternate program appears to be impossible since it would eliminate the high quality catalytically cracked stocks for direct blending.

The lack of availability of aromatics to fulfill the requirements of the alternate program leaves only the ethers and aromatic amines for consideration as possible substitutes for cumene. From the comparison presented in Appendix A of twenty-seven aromatics and twenty-three ethers, it appears that the better ethers and aromatics are about equal in rich mixture antiknock performance. On the basis of the limited data available, the requirements for the better ethers; methyl tert-butyl ether, ethyl tert-butyl ether, isopropyl tert-butyl ether, and diisopropyl ether, are roughly about the same as for toluene and xylene. For the present and alternate programs, these are 10,000 to 11,000 and 34,000 to 35,000 barrels per day, respectively. These ethers are produced by treating the olefin with the appropriate alcohol. Isobutylene used for ether production would have to come from supplies normally used for producing aviation alkylate or hydro-codimer. Although these ethers all have better knock-limited performance than aviation alkylate, lack of service experience and lack of well-developed production facilities do not allow a complete evaluation of the ethers as cumene substitutes for either present or alternate programs.

Lack of availability of aromatics and lack of information on ethers to fulfill the requirements of the alternate program leaves only the

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aromatic amines as possible blending agents to acquire the high rich mixture ratings at the 3.0 ml TEL per gallon level. The aromatic amines are 3.5 to 5.0 times more effective in enhancing rich mixture quality than the aromatics from which they are derived; therefore, the quantities required are reduced by that ratio.

Appendix B of this report summarizes most of the information available on the aromatic amines, which in the past have been investigated as possible additives for aviation gasoline. The effectiveness of the aromatic amines in improving rich mixture rating is a function of the rich rating level to which the gasoline is blended and is a function of the concentration of the aromatic amine in the finished gasoline. For example, a 1% concentration of mixed xylidines (CS) at the Grade 130 level has an approximate F-4 blending index number of 1000. On the other hand, a 3% blend of CS at a 145 performance level has an F-4 blending index number of about 650. Since this variation in blending index number is not typical of other aromatic amines, objections have arisen to treating the blending values of amines on the basis of "blending INEP." However, extensive experimentation during the past war indicated that this was a reasonably close approach when adapted to fuels in the 100 to 150 performance number range. It must be recognized, however, that the quantity of aromatic amines that would be required under emergency conditions may not be as specifically stated as the requirement for aromatics. If all Grade 145 were produced, one quantity would be required; whereas, if Grade 130 were produced, another quantity would be required. These two cases do, however, represent extremes and requirement figures for aromatic amines will be based upon them.

Considering, among other factors, volatility characteristics, the amines most adaptable to aviation fuel blending are limited to mono methyl aniline, toluidines, and xylidines. Past experience is available on both the manufacture and use of mono methyl aniline and xylidines in high quality aviation gasolines. Subsequent comment will be limited largely to these two materials although, in any long-range study, toluidines should be considered for possible use in place of them.

To replace 10,000 and 32,000 barrels of cumene with mono methyl aniline (MMA) in a Grade 145 fuel, there would be required approximately 1600 and 5700 barrels, respectively. At the Grade 130 level the amount of MMA required would be 1300 and 9800 barrels for the present and alternate programs, respectively. Benzene would be a normal intermediate in the production of MMA. This component is not available, but in this case the special measure may be justified to fractionate cyclohexane and methyl cyclopentane from gasoline, dehydrogenate to benzene, nitrate and reduce to aniline, and methylate. The dehydrogenation, nitration and reduction steps would be common practice. There is information that the methylation can be carried out by a simple catalytic process (See Appendix B). The cost of the facilities and the metal requirement are believed to be reasonable and should be estimated.

To replace with xylidine 10,000 and 32,000 barrels of cumene would require about 1900 and 6900 barrels, respectively, at the Grade 145 level. At the Grade 130 level, 1500 and 11,700 barrels, respectively, would be required for the present and alternate programs. The quantity of xylene required for either of these programs could be made available from catalytically cracked stocks by the installation of fractionating and extraction facilities. Methods for producing mixed xylidines from petroleum xylene are well known. During the past war, installations designed to produce approximately 4000 barrels per day were available and peak production rates approaching 2000 barrels per calendar day were attained. This experience would provide information on investment and metal requirements should expansion in the production of mixed xylidines appear attractive.

On the basis of the laboratory data available, toluidine requirements would be roughly equivalent to those stated above for mono methyl aniline. The basic intermediate required for its manufacture would be toluene. It is believed that in an emergency present productive capacity would barely be sufficient to meet initial requirements for toluene. Additional toluene production facilities could, however, be made available to the extent required should they be deemed necessary. No problem is anticipated in the processing required to convert the toluene to toluidine.

There are listed in the following table the approximate percentages of mono methyl aniline and xylidines that would be required in the finished fuel under the present and alternate programs to attain the 130 and 145 rich mixture performance number levels. The production figures indicated below, 240,000 barrels per day and 520,000 for Grades 145 and 130, respectively, represent maximum alternate quantities that could be produced from currently installed facilities under emergency conditions. Concurrent production of both grades, at some total figure intermediate between 240,000 and 520,000 barrels per day, would not change these percentage figures but would obviously affect the total quantity of the amines required. Under the present program, the concentration of amines would vary from a minimum of 0.25% at the 130 PN level to a maximum of 0.8% at the 145 PN level. In the alternate program, using 3.0 ml TEL per gallon, the concentration of amines would vary from approximately 1.9% at the 130 PN level to nearly 3% at the 145 PN level.

| Alternate Quantities | Present Program | | | | Alternate Program | | | |
|----------------------|-----------------|------|------|------|-------------------|------|------|--------|
| | 4.6 ml TEL/Gal | | | | 3.0 ml TEL/Gal | | | |
| | % MMA | B/D | % CS | B/D | % MMA | B/D | % CS | B/D |
| 240,000 B/D 145 PN | 0.65 | 1600 | 0.8 | 1900 | 2.4 | 5700 | 2.9 | 6,900 |
| 520,000 B/D 130 PN | 0.25 | 1300 | 0.3 | 1500 | 1.9 | 9800 | 2.3 | 11,700 |

No mention has been made to this point on the effect of the amines on the lean mixture performance of the fuel. It appears to be the consensus that the F-3 rating of a fuel is not indicative of full-scale performance under lean mixture conditions, particularly in the engines of newer design which will comprise most of the reciprocating engines in

use in another war. F-3 ratings on the various amine-containing blends may, however, be predicted. Substitution of an amine for cumene in the present program (4.6 ml TEL per gallon) would not affect the 100 and 115 F-3 performance number ratings of Grades 100/130 and 115/145, respectively. The exclusive use of an amine to maintain the 130 and 145 PN levels in the alternate program (3.0 ml TEL/gallon) will result in an F-3 rating of 105 PN on the 145 Grade and 90 PN (97 octane number) on the 130 Grade. These ratings are not considered indicative of the full-scale performance under lean mixture conditions (See Appendix B).

Mention of the source of information on blending values of mixed xylidines and mono methyl aniline seems to be advisable. During the past war, rather extensive blending information was obtained on mixed xylidines in concentrations varying between 0.5 and 5.0% in fuels with base performance numbers varying between values below 100 and as high as 160. These data were correlated by the Aviation Gasoline Advisory Committee to the Petroleum Administration for War and are presented in Report No. 5, dated June 1, 1944, submitted by the Subcommittee on Blending Octane Numbers. Less data are available on mono methyl aniline. Information from various sources indicates, however, that in normal concentrations it is about 1.2 times as effective as mixed xylidines (See Appendix B). It has been arbitrarily assumed that its blending value will vary with concentration and with the performance number of the base fuel into which it is blended in a manner proportional to those variations of mixed xylidines.

Performance of Aromatic Amines. The use of aromatic amines during World War II raised a number of questions as to their suitability with reference to engine performance which must be settled before they can become a part of any definite aviation fuel production plan. There has been a limited amount of experience obtained by the Air Force since the war which is somewhat encouraging from the performance standpoint. The Air Force reports that approximately 44,000,000 gallons of Grade 100/130 fuel containing from 0.06 to 0.84% mono methyl aniline was recovered from British storage during 1947 and distributed rather widely throughout the continental United States for use in service equipment. No apparent operating difficulties have been encountered. In addition, during the past year approximately 15,000,000 gallons of Grade 100/130 containing 0.8 to 1.0% CS was used in both continental United States and European operations with no reported service difficulties.

In spite of this experience, it appears that a more thorough investigation of the performance of amines in fuels used in the most advanced engines is imperative. This study should include both the power plants of principal interest and the important operation conditions -- especially protracted operation at high power and at reduced powers required for long-range cruising. An adequate test schedule and a review of available information should be undertaken to resolve possible disadvantages which

may arise from the presence of aromatic amines in the fuel from the standpoint of:

- 1) Mal-distribution
- 2) Deposits
- 3) Pre-ignition
- 4) Attack upon rubber and synthetics
- 5) Corrosive attack
- 6) Storage stability
- 7) Toxicological effects

Each of the factors has been discussed in Appendix B, but will be reviewed briefly at this point.

The amines have relatively high boiling points; 383° F for MMA and 421° F for CS. Under many engine operating conditions these materials will probably not be completely vaporized and may not be completely mixed with the air-fuel mixture being distributed to the several cylinders. Low concentrations in certain cylinders would, of course, lead to detonation.

A tendency toward deposit, sludge, and varnish formation with increased propensity toward ring sticking and spark plug fouling is also largely a function of the volatility characteristics of the amines. It is conceivable that they may not be completely vaporized prior to combustion in the cylinder and would, therefore, deposit on valves, rings, and spark plugs. Any mal-distribution effects would, of course, intensify deposit difficulties in certain cylinders.

No general statement regarding preignition limits of aromatics and aromatic amines can be made inasmuch as the individual members of a class of organic compounds may differ in preignition characteristics. Full-scale single-cylinder engine data indicate that toluene and mixed xylenes have preignition limits equal to or higher than those of triptane or S reference fuel. Small-scale engine tests on 2-percent amine blends with AN-F-28 (28-R) fuel indicate that xylidines and monomethyl-aniline have little or no effect on the preignition limit of 28-R. At lean fuel-air ratios only N-methyltoluidines do appear to lower the preignition limit of 28-R. It is emphasized that preignition limits vary with engine severity.

Solvency characteristics of amines are generally considered to be 5 to 10 times as great as those of the aromatics from which they are derived. When substantially aromatic-free post-war gasolines caused shrinkage and consequent malfunctioning or leakage of synthetic components of the fuel system, about 1% CS was added to cause swelling and eliminate the difficulties. With higher concentrations of CS there is, therefore, some possible danger from attack upon synthetic rubber and plastic materials in the fuel system. Considering the improvements that have been made during the last war and subsequent to that time in

solvent resistant characteristics of synthetics, it is unlikely that any great difficulty in this respect will be encountered. It is a factor, however, that should be investigated in any long-range program.

Concern over corrosive attack on copper and other materials employed in fuel systems seems to stem back to the time when experimental work was conducted with aniline as an antiknock agent in automotive engine fuels. There was no reported difficulty in this respect during the past war with the use of amine blends. This is, however, another factor which should be investigated in the course of any long-range study.

Previous experience with amine blends has indicated that some storage stability problems do arise. These problems involve color changes, gum formation, and extraction of the amines from the gasoline by water where the product is stored over water. Considerable information has been obtained on all of these factors and it should be reviewed (See Appendix B).

CS is a very toxic material and its effects upon the human body have been definitely established. It is, however, no more harmful than tetraethyl lead. Its physiological effects are not similar to lead and the effects of the two are not additive. The blending of amines has been carefully studied and presents no problem as long as they are handled with care. No ill effects should be anticipated in handling blends in the manner prescribed for any fuel containing tetraethyl lead.

An adequate schedule to cover the engine performance characteristics listed above should include the following:

- 1) Multi-cylinder ground running duplicating the known typical operating conditions
- 2) Single cylinder exploration of any questionable performance revealed by 1)
- 3) Flight tests verifying the results of 1) if warranted by the ground tests and other studies
- 4) Operational tests if all other tests are sufficiently favorable.

CONCLUSIONS

From the production and availability standpoint, it appears that aromatic amines should be considered as a component of high octane number aviation fuels in case of an emergency if the Military Service's aircraft operations require that the lead content be dropped from 4.6 to 3.0 ml per gallon. Mixed xylydines appear to be most attractive from the availability standpoint but mono methyl aniline has the advantage

of being somewhat more effective, more volatile, and more stable in aviation fuel blends. Detailed information on toluidines is not available and should be developed if any long-range program is envisaged.

If the lead content can be maintained at the 4.6 ml per gallon level, it appears possible to augment supplies of toluene or xylenes to replace cumene in meeting rich mixture requirements.

The requirements for ethers are about the same as for toluene and xylene as components to improve rich mixture performance. Certain ethers gave an even better knock-limited performance than aviation alkylate. Because of the lack of service experience and lack of well-developed production facilities a complete evaluation of ethers cannot be made at this time.

From the engine performance standpoint a rather extensive program must be undertaken to establish performance of amine-containing blends in the most advanced engines under various types of operating conditions. The principal factors to be investigated are the effect of the high boiling characteristics of amines, the tendencies toward increased deposits, preignition tendency, attack of non-ferrous metals and synthetic materials in the fuel induction system and stability of the fuel in storage.

APPENDIX A

Aromatics and Ethers in Aviation Fuels

INTRODUCTION

A study is being conducted by the Subcommittee on Aircraft Fuels of the NACA Committee on Power Plants to determine the possible blending agents or additives that may be substituted for cumene (isopropylbenzene) in future aviation fuels. The need for this study arises from the fact that the limited availability of benzene in future emergencies will reduce the quantity of cumene that can be made available for aviation fuels - benzene being the starting material in preparation of cumene. Other aromatics that may be used in place of cumene for aviation fuels are few in number when volatility and availability restrictions are considered. For this reason it has been necessary to include in this study the possibility of using ethers and additive-type compounds, such as aromatic amines, as cumene substitutes.

Accordingly it is the purpose of this appendix to present a summary of information available for aromatic hydrocarbons and ethers. The subject of aromatic amines is treated in Appendix B.

DISCUSSION OF RESULTS

The NACA laboratories conducted investigations of twenty-seven aromatics and twenty-three ethers. Antiknock data and physical properties for compounds in these classes are presented in tables I to IV. The antiknock data presented in tables I and III were determined in the F-3 and F-4 engines. All of the aromatics and ethers were evaluated in blends with leaded and unleaded S reference fuel and in blends with a prepared base fuel containing 87.5 percent (by volume) isooctane plus 12.5 percent n-heptane with the final blends leaded to 4 ml per gallon. For the purposes of this discussion only the 25 percent blends of ether or aromatic with the base fuel were considered, inasmuch as antiknock ratings were determined for all compounds at this concentration level. The nominal performance grade of the base fuel was about 120/112.

Aromatics

Antiknock Performance. An idea of the relative lean antiknock characteristics of the aromatic hydrocarbons can be obtained from an examination of the F-3 data for 25-percent blends in table I. Fifteen aromatics improved the performance of the base fuel, but in no case did this improvement exceed 7 performance numbers. Of the aromatics in this group, 1,3,5-trimethylbenzene and tert-butylbenzene appear to be the most desirable aromatics from consideration of antiknock value alone.

Both of these hydrocarbons are about 4 to 10 performance numbers better than cumene, xylenes (meta and para), and toluene, the aromatics generally accepted as being more readily available.

As contrasted to the F-3 data, the 25-percent additions of aromatic in the base fuel have caused considerable improvement in F-4 performance (table I) of from 112 performance number for the base fuel to about 175 for the best aromatic blend. The 1,3,5-trimethylbenzene blend at F-4 conditions is still one of the highest performance blends but the tert-butylbenzene blend which showed up well in the F-3 tests is exceeded in knock-limited performance by a number of other aromatic blends. Other than 1,3,5-trimethylbenzene, the best aromatics shown are 1-methyl-3-ethylbenzene, 1,3-dimethyl-5-ethylbenzene, 1-methyl-3-tert-butylbenzene, 1-methyl-4-tert-butylbenzene, 1-methyl-3,5-diethylbenzene, and 1,3,5-triethylbenzene. These aromatic are 10 to 25 performance numbers better than cumene, xylenes (meta and para), and toluene.

Physical Properties. Although several aromatics possess knock-limited performance characteristics equal to or better than those of cumene, only 1,3-dimethylbenzene (m-xylene), 1,4-dimethylbenzene (p-xylene), ethylbenzene, and toluene have boiling points (table II) in the range defined by Specification AN-F-48. In an analysis of existing experimental data, the Esso Laboratories have considered the effects of additions of toluene, xylenes, and cumene on fuel volatility. Isopentane was included in this study, inasmuch as this component would be added in sufficient quantity to adjust the vapor pressure of the final blend to the specified value (7 lb/sq inch).

(a) Volatility. - Addition of straight aromatics to aviation fuel does not increase the ASTM 10-percent point greatly. The various aromatics have roughly equivalent effects within the accuracy of the data. If the aromatic is added in conjunction with sufficient isopentane to maintain 7 pounds per square inch Reid vapor pressure, the ASTM 10-percent point of the fuel is practically unchanged since the effects of the isopentane and aromatic balance out.

The effect on ASTM 50-percent point of adding toluene is a function of the 50-percent point of the fuel before addition of toluene. The lower the 50-percent point of the fuel, the more it is elevated by adding toluene, as would be expected. Xylenes and cumene increase the 50-percent point to a greater extent than toluene. The influence of these compounds on the 50-percent point correlates with the difference between the ASTM 50-percent and 90-percent points, with a few exceptions. Apparently, since these compounds are considerably higher boiling than the ASTM 50-percent temperature, their major effect in the 50-percent region is to displace the curve laterally to the left. Thus, the greater the slope of the distillation curve at 50-percent, the more the 50-percent point is increased by adding a given amount of xylene or cumene.

Aviation fuel containing greater than 5 volume percent cumene has an ASTM final boiling point of approximately 360° F regardless of the final boiling point before addition of cumene. This is attributed to the fact that commercial cumene which was used in most if not all the blends included in this correlation, contains an appreciable but varying proportion of material boiling above 360° F. However, since pure cumene has a true boiling point of 306° F, removal of a small proportion of high boiling material from commercial cumene will reduce substantially its effect on ASTM final boiling point. Addition of either toluenes or xylenes to aviation fuel appears to have no consistent effect on the final boiling point.

Although the correlations given here are not firm due to the relatively small amount of data available, they are fairly consistent, and should be useful for purposes of approximation. For example, if it is desired to add 20 volume percent of a 7 pounds per square inch Reid vapor pressure "aromatic blending agent" consisting of xylenes and isopentane to a typical aviation fuel, the effect on ASTM distillation could be estimated to be

| ASTM | NET EFFECT (°F) |
|------------------|-----------------|
| 10 percent point | -1 |
| 50 percent point | +9 |
| 90 percent point | +17 |

(b) Other Physical Properties. - In addition to volatility characteristics, other properties of the aromatics enter into any considerations of their suitability as aviation fuel blending agents. Freezing points and heats of combustion are presented in table II, together with boiling points for the aromatic hydrocarbons. A number of the aromatics that have good antiknock characteristics (table I) have high freezing points and all of the aromatics have heats of combustion slightly lower than paraffinic types.

More important than either heat of combustion or freezing point is the solubility of water in aromatic fuel blends. For the aromatics in table II water solubility data are unavailable; however, as an example of how serious this factor may be in use of aromatic blends, one literature source states that the aromatics dissolve about ten times as much water as normal gasolines. Still another source indicates that the addition of 25 percent cumene to a straight-run stock increased the percent by weight of dissolved water from 0.007 to 0.012.

For the concentrations in which aromatics might be utilized in future aviation fuels, the properties discussed in the preceding paragraphs offer no insurmountable obstacles. In this connection, it may

be recalled that during World War II some AN-F-28 fuels containing aromatic concentrations as high as 20 percent were used.

Availability. No aromatic materials boiling in a higher range than cumene can be considered for aviation fuels because of fuel volatility limitations in the AN-F-48 specification. For this reason only ethylbenzene, *m*-xylene, *p*-xylene, toluene, and benzene offer possibilities as substitute blending agents for cumene.

In an analysis of the availability of these materials made at the Soccony-Vacuum Laboratories, it was assumed that ethylbenzene could be produced by the alkylation of benzene with ethylene, using equipment and processes similar to those required for the manufacture of cumene. Catalytically cracked stocks have been considered as a source of toluene-xylene mixtures which might be concentrated by extraction. Hydroforming combined with extraction has been considered as a source of toluene. Benzene should probably be eliminated as a possible replacement on the basis of the fact that inadequate quantities would be available from sources other than petroleum and suitable substitutes such as toluene and xylenes may be obtained from petroleum with lower investments.

The following table summarizes the cost of replacing 10,000 barrels per day of cumene in aviation gasoline with other suitable aromatics.

| Aromatic blending agent | Processing required | Raw Stocks | | Investment, dollars | Metal requirement, tons |
|-------------------------|-------------------------------------|-----------------------|--------------------------|---------------------|-------------------------|
| | | Type | B/D | | |
| Ethylbenzene | Ethane-ethylene fractionation | Benzene Ethylene | 9,100 900,000 lb/D | 6,000,000 | 5,000 |
| Toluene and xylenes | Solvent extraction | Cat. cracked gasoline | 175,000 | 40,000,000 | 25,000 |
| Toluene | Hydroforming and solvent extraction | Virgin naphtha | 110,000 | 110,000,000 | 90,000 |

Approximately 9,100 barrels per day of benzene would be required to produce 11,200 barrels of ethylbenzene which would be equivalent to 10,000 barrels per day of cumene as a rich mixture blending agent. The installation of fractionating facilities would be required to segregate about 900,000 pounds per day of ethylene in an ethane-ethylene mixture. This would involve an investment of \$6,000,000 and require 5,000 tons of metal.

Since only 7,500 barrels of benzene will produce 10,000 barrels of cumene, a source of an additional 1,900 barrels per day of benzene is necessary. Considering the multitude of essential uses of benzene in times of emergency, this may be difficult.

The average catalytically cracked gasoline has been calculated to contain approximately 3 percent toluene and 5 percent mixed xylenes. Solvent extraction equipment could be installed to segregate these aromatics at an investment cost of \$40,000,000 using 25,000 tons of metal. To produce the equivalent of 10,000 barrels per calendar day of cumene, 175,000 barrels per day of catalytically cracked gasoline would be required as a feed stock. Prefractionation prior to extraction would be required to segregate toluene and xylene fractions. Fractionation would follow extraction to eliminate the low rating o-xylene.

Eleven thousand barrels per day of toluene would be equivalent to 10,000 barrels per day of cumene. The production of this quantity would require the investment of \$110,000,000 and would require 90,000 tons of metal. One hundred and ten thousand barrels per day of feed stocks, for the most part selected straight run naphthas, would have to be provided.

As a point of interest, the country-wide production capacity for toluene from petroleum sources under emergency conditions is currently approximately 13,000 barrels per calendar day. It has been assumed that this entire amount would be required for the manufacture of explosives and other essential war materials. Fulfilling the requirements of aviation gasoline for aromatics by the use of toluene would nearly double today's potential production. It is generally felt that availability of suitable feed stocks might be limiting and, under any circumstances, rather extensive use of transportation would be required to transport feed stocks from their point of production to the location of the hydroformer units.

Ethers

Antiknock Performance. Antiknock data for 25-percent ether blends are shown in table III. Both aliphatic and aromatic ethers were examined.

Of the blends shown, the isopropyl tert-butyl ether blend gave the highest performance number at F-3 conditions. Next in order were ethyl tert-butyl ether and methyl tert-butyl ether, about 6 performance numbers lower. None of the aromatic ethers improved the performance of the base fuel.

For the F-3 conditions the best ether blend was about 30 performance numbers better than the base fuel, whereas in table I it was shown that the best aromatic blend was only 7 performance numbers better than the

base fuel. The best ether, isopropyl tert-butyl ether, was 26 to 32 performance numbers better than cumene, xylenes (meta and para), and toluene.

At F-4 conditions (table III) the blend containing methyl tert-butyl ether had the highest performance number and showed about the same improvement over the base fuel as that found with the best aromatic, 1,3,5-trimethylbenzene. In contrast to the results obtained at F-3 conditions, the F-4 investigation indicated that the aromatic ethers offer considerable improvement over the base fuel. Of the aromatic ethers examined, m-methylanisole and isopropyl phenyl ether were second only to methyl tert-butyl ether in F-4 performance. However, with the exception of methyl tert-butyl ether all of the better ethers were exceeded in performance by a number of aromatics in the F-4 engine.

In addition to the ethers presented in table III, diisopropyl ether has recieved attention in past years but the available data are not directly comparable with the data in table III. In general, however, the antiknock performance of diisopropyl ether does appear to be of the same magnitude as the performance of methyl tert-butyl ether, ethyl tert-butyl ether, and isopropyl tert-butyl ether.

Physical Properties. The general suitability of ethers as blending agents in aviation gasoline must be considered on the basis of volatility, heat of combustion, water tolerance, and storage stability.

(a) Volatility Characteristics. - The dialkyl ethers listed in table IV boil within the boiling range of AN-F-48 aviation gasoline so that the inclusion of dialkyl ethers would not noticeably influence the volatility characteristics of the finished fuel.

The Reid vapor pressure of methyl tert-butyl ether has been measured to be 8.8 pounds per square inch. A virgin base stock with a Reid vapor pressure of 5.9 pounds per square inch when blended with 20 percent methyl tert-butyl ether gave no appreciable increase in Reid vapor pressure and 40 percent ether with the virgin base gave a Reid vapor pressure of 7.1 pounds per square inch.

On the other hand, the aromatic alkyl ethers boil above the end point of the AN F-48 specification. Anisole boiling at 308° F might be considered to be a borderline case, but the inclusion of any aromatic ethers in 10 percent concentrations would require raising the 90 percent point of the fuel above the present specification limit.

(b) Heat of Combustion. - The heats of combustion of ethers are lower than for hydrocarbons. For example, methyl tert-butyl ether with a net heat of combustion of 15,200 Btu per pound could not be tolerated in large quantities if the minimum heating value of 18,700 Btu per pound is to be maintained. However, methyl tert-butyl ether blends up to 20

percent in hydrocarbon stocks show no increased indicated specific fuel consumption when evaluated in small-scale single cylinder engines. Also, full-scale single-cylinder engine tests indicate that 10 percent ether blends do not increase specific fuel consumption.

(c) Water Tolerance. - When considering the suitability of ethers as blending agents for aviation gasoline, both the tendency for water to dissolve in ethers and the tendency for ethers to dissolve in water must be considered. Unfortunately, reliable data on water tolerances of ethers are meager. However, one study has compared the quantity of water that will be dissolved by blends of methyl tert-butyl ether in a straight run aviation base stock and blends of cumene in the same base stock. The data are shown in the following table.

SATURATED WATER CONTENT AT 77° F OF STRAIGHT-RUN AVIATION
BASE STOCK CONTAINING VARYING PERCENTAGES OF METHYL
tert-BUTYL ETHER OR CUMENE

| Blend composition, weight. percent | | Percent by weight of dissolved water |
|------------------------------------|---------------------------------|---|
| Base stock | Cumene | |
| 100 | | |
| 95 | 5 | |
| 90 | 10 | |
| 75 | 25 | |
| 50 | 50 | |
| Base stock | Methyl <u>tert</u> -butyl ether | |
| 97 | 3 | |
| 95 | 5 | |
| 90 | 10 | |

This table indicates the maximum quantity of water that would be dissolved in the fuels at the temperature indicated. The actual quantity of water dissolved during service operations would be dependent upon the manner in which the fuel was stored and handled.

The tendency of diisopropyl ether blends to dissolve water has also been studied and some data are shown below.

| Fuel | Milliliters of water dissolved per 100 milliliters of fuel | |
|--|---|-------|
| | 32° F | 77° F |
| Aviation gasoline (paraffinic) | 0.006 | 0.007 |
| Aviation gasoline with 40 percent diisopropyl ether | .062 | .085 |

At the low ambient temperatures which may be encountered in service, water tends to separate and form ice crystals, which may clog fuel line filters if the ice particles are of sufficient size to be held on the filters. The quantity of ice formed at low temperatures will be directly proportional to the water dissolved at higher temperatures. Therefore, ether blends might present more of a problem than hydrocarbon blends under conditions that result in the formation of ice in the fuel.

One method of alleviating the problem of ice crystal formation is to add to the fuel a material that acts as a freezing point depressant for the water. Methanol has been added in a concentration of 0.5 percent with 40 percent diisopropyl ether in experimental aviation gasoline. Cooling of this mixture caused the water to separate but due to the presence of the methanol no ice crystals were formed. Therefore, it is indicated that small amounts of freezing point depressants might be effective in eliminating the problem of ice crystal formation.

The solubility of ethers in water will affect the feasibility of over-water storage for gasolines containing ethers. Methyl tert-butyl ether is reported to be soluble in water to the extent of 4.8 grams of ether per 100 grams of solution at 68° F. Diisopropyl ether is soluble to the extent of 0.65 weight percent at 77° F. Unfortunately, these data are not from the same source and may not be comparable. Water extraction of a gasoline containing 10 percent diisopropyl ether has indicated that after three extractions, only 0.4 percent of the ether was removed from the gasoline. It would appear that diisopropyl ether would be suitable as a blending component so far as overwater storage is concerned, but methyl tert-butyl ether might be questionable. However, the subject should be more fully investigated before a decision can be reached on the feasibility of overwater storage.

(d) Storage Stability. - Certain ethers are known to form peroxides readily during storage if they are not properly inhibited. Supposedly, peroxide formation would be deleterious from two points of view. First, the presence of small concentrations of peroxides depreciate the antiknock effectiveness of fuels very drastically. A fuel containing sufficient peroxides would reduce the performance level of the fuel and might constitute a serious operational problem.

The second item to be considered is the tendency toward gum formation. Supposedly, the presence of peroxides would indicate the initial step in the decomposition of a fuel during storage.

Actual experience with some dialkyl ethers such as methyl tert-butyl ether and diisopropyl ether has shown that, when properly inhibited, aviation gasoline blends containing ethers are stable during storage. Therefore, no storage problems due to deterioration of the performance level of the fuel or to gum formation are anticipated. However, very extensive tests would be required before the point is beyond doubt.

Availability. The ethers of greatest interest from the standpoint of antiknock performance and volatility are methyl tert-butyl ether, ethyl tert-butyl ether, isopropyl tert-butyl ether and diisopropyl ether.

Methyl tert-butyl ether is prepared by the treatment of methanol with isobutylene in the presence of sulfuric acid. Several thousand gallons of the ether were produced on a pilot plant scale during World War II. The process apparently is similar mechanically to an alkylation process and the ether could be produced on a large scale. The methanol required for the production of suitable quantities of methyl tert-butyl ether would probably be larger than the methanol required for the production of N-methyl aromatic amines. An accurate comparison of methanol requirements depends upon the yield of monomethyl aromatic amine obtained by treatment of the amine with methanol. The well-known methods for this reaction give fairly low yields of the monomethyl product. Unless the yields can be raised, it is possible that the methanol requirement would be about the same for the required production of methyl tert-butyl ether as for the production of a monomethyl aromatic amine such as monomethyl aniline.

Isobutylene used for methyl tert-butyl ether production would come from supplies normally used for producing aviation alkylate or hydrocodimer. The isobutylene required to produce 500 barrels of methyl tert-butyl ether would produce about 700 barrels of C_4 alkylate.

Since the methyl tert-butyl ether gives a higher knock-limited performance than the alkylate under both lean and rich operating conditions, the use of the isobutylene for ether production may be justified. A satisfactory evaluation would require detailed study and would depend upon the availability of other blending stocks and the performance level of the fuel required.

The production of ethyl tert-butyl ether involves the use of ethyl alcohol and isobutylene. In this case the ratio of ether produced to potential C_4 alkylate would be more favorable than in the case of methyl tert-butyl ether. The isobutylene required to produce 500 barrels of ethyl tert-butyl ether would be equivalent to the production of 590 barrels of C_4 alkylate.

The production of isopropyl tert-butyl ether involves the use of propylene and isobutylene and the production of diisopropyl ether involves the reaction of propylene with water in the presence of sulfuric acid. Propylene is again a material that is normally used for the production of aviation alkylate and a thorough study would be required to determine whether the propylene would be most profitably used in the hydrocarbon fuel or the ether.

SUMMARY REMARKS ON AROMATICS AND ETHERS

The available data indicate that from consideration of anti-knock performance alone, 1,3,5-trimethylbenzene and methyl tert-butyl ether appear to be the most desirable of the aromatics and ethers. However, other compounds in these classes are certainly worthy of consideration.

Insofar as general usage of aromatics and ethers is concerned, properties other than antiknock performance must be considered. In the following paragraphs, the characteristics of these two classes of compounds have been compared.

1. Possibly the most important advantage of the aromatics is the fact that aromatic blending agents have been used successfully in aircraft fuels for a number of years and no insurmountable obstacles have been encountered.
2. The dialkyl ethers are superior to the best aromatics in lean-mixture antiknock characteristics.
3. The better ethers and aromatics are about equal in rich-mixture antiknock characteristics.
4. Only a few aromatics have boiling points within the limits of the AN-F-48 specification and these particular aromatics are not the best from antiknock considerations. The dialkyl ethers which were the best ethers from the standpoint of antiknock performance boil within the range of the specification; consequently, the use of ethers in aviation fuels should not present the problems associated with high-boiling constituents.
5. The ethers have lower heats of combustion than aromatics; however, for the concentrations that might be used in aircraft fuels, it is questionable whether increased fuel consumption with ether blends would be observed in service.
6. The water solubility of the aromatics is somewhat less than that of the ethers. The solubility of water in ethers and the solubility of ethers in water could be a serious problem and should be investigated thoroughly.
7. Production of suitable ethers for aviation fuel blends would require olefin gases that were used during World War II to produce aviation alkylate or hydro-codimer. Methanol would also be required for the production of methyl tert-butyl ether. Production methods for aromatics are well developed. However, expansion of facilities to provide the necessary quantities of aromatics would entail large investments and metal requirements. Sufficient data are not available to permit a conclusion as to the investment required to produce ethers.

TABLE I - F-3 AND F-4 PERFORMANCE NUMBERS OF AROMATIC BLENDS^a

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| Aromatic | F-3 | | | | | | F-4 (F/A=0.11) | | | | | |
|--|---|----|-------------|-----|---|-----|----------------|-----|-----|------|--|--|
| | Volume-percent aromatic in S reference fuel | | | | Volume-percent aromatic in mixed base fuel ^b | | | | | | | |
| | Unleaded | | 4ml TEL/gal | | 4ml TEL/gal | | | | | | | |
| | 10 | 20 | 10 | 20 | 10 | 25 | 50 | 10 | 25 | 50 | | |
| Benzene | 96 | 92 | --- | --- | 121 | 116 | 97±6 | 123 | 139 | 174 | | |
| Methylbenzene (Toluene) | -- | 94 | --- | 139 | 121 | 117 | 113 | 126 | 151 | >290 | | |
| Ethylbenzene | 97 | 95 | --- | 138 | 120 | 119 | 106 | 128 | 154 | >260 | | |
| 1,2-Dimethylbenzene (o-Xylene) | 93 | 86 | 136 | 118 | 113 | 105 | 84 | 102 | 100 | 111 | | |
| 1,3-Dimethylbenzene (m-Xylene) | 100 | 98 | 150 | --- | 125 | 123 | 122 | 129 | 166 | 297 | | |
| 1,4-Dimethylbenzene (p-Xylene) | 98 | 99 | 148 | 138 | 125 | 122 | --- | 128 | 163 | <300 | | |
| n-Propylbenzene | 96 | 93 | 146 | --- | 126 | 122 | 118 | 125 | 152 | 205 | | |
| Isopropylbenzene (Cumene) | 98 | -- | --- | --- | 122 | 122 | --- | 131 | 152 | 283 | | |
| 1-Methyl-2-ethylbenzene (o-Ethyltoluene) | -- | 86 | --- | 124 | --- | 107 | --- | --- | 122 | --- | | |
| 1-Methyl-3-ethylbenzene (m-Ethyltoluene) | -- | 95 | --- | 142 | --- | 124 | --- | --- | 168 | --- | | |
| 1-Methyl-4-ethylbenzene (p-Ethyltoluene) | 96 | 88 | --- | --- | 122 | 120 | --- | 132 | 159 | 213 | | |
| 1,2,3-Trimethylbenzene | -- | 85 | --- | 115 | --- | 105 | --- | --- | 102 | --- | | |
| 1,2,4-Trimethylbenzene | 91 | 87 | 141 | 121 | 113 | 101 | 97 | 107 | 113 | 146 | | |
| 1,3,5-Trimethylbenzene (Mesitylene) | -- | -- | 150 | --- | 123 | 127 | --- | 137 | 168 | >300 | | |
| n-Butylbenzene | 96 | 89 | --- | --- | 118 | 118 | 111 | 121 | 133 | 156 | | |
| Isobutylbenzene | 97 | 93 | --- | --- | 120 | 119 | 116 | 123 | 144 | 174 | | |
| sec-Butylbenzene | 96 | 93 | 146 | 138 | 123 | 122 | 112 | 123 | 146 | 176 | | |
| tert-Butylbenzene | 98 | 99 | 151 | 142 | 125 | 127 | 126 | 133 | 161 | 286 | | |
| 1-Methyl-4-isopropylbenzene (p-Cymene) | 98 | 95 | --- | --- | 126 | 123 | 113 | 128 | 158 | 223 | | |
| 1,2-Diethylbenzene (o-Diethylbenzene) | -- | 84 | --- | 125 | --- | 107 | --- | --- | 122 | --- | | |
| 1,3-Diethylbenzene (m-Diethylbenzene) | 96 | 92 | 145 | --- | --- | 123 | --- | 134 | 164 | 225 | | |
| 1,4-Diethylbenzene (p-Diethylbenzene) | -- | 94 | --- | 136 | --- | 119 | --- | --- | 163 | --- | | |
| 1,3-Dimethyl-5-ethylbenzene | -- | 95 | --- | 140 | --- | 124 | --- | --- | 171 | --- | | |
| 1-Methyl-3-tert-butylbenzene (m-tert-Butyltoluene) | -- | 93 | --- | 141 | --- | 125 | --- | --- | 169 | --- | | |
| 1-Methyl-4-tert-butylbenzene (p-tert-Butyltoluene) | -- | 97 | --- | 142 | --- | 124 | --- | --- | 176 | --- | | |
| 1-Methyl-3,5-diethylbenzene (3,5-Diethyltoluene) | -- | 95 | --- | 140 | --- | 126 | --- | --- | 171 | --- | | |
| 1,3,5-Triethylbenzene (sym-Triethylbenzene) | -- | 93 | --- | 140 | --- | 122 | --- | --- | 170 | --- | | |

^aPerformance numbers greater than 161 were determined as follows:

$$\text{Performance number} = \frac{\text{imep of blend}}{\text{imep of S+6 ml TEL/gal}} \times 161$$

^bThe mixed base fuel contained 87.5 percent (by volume) S reference fuel and 12.5 percent n-heptane. This blend was leaded to 4 ml tetraethyl lead per gallon and had F-3 and F-4 performance numbers of 120 and 112, respectively.

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TABLE II - PHYSICAL PROPERTIES OF AROMATIC HYDROCARBONS^a

| Aromatic | Boiling point (°F) | Freezing point (°F) | Heat of combustion (Btu)/(lb) |
|------------------------------|-----------------------|------------------------|-------------------------------------|
| Benzene | 176.19 | +41.96 | 17,259 |
| Methylbenzene | 231.12 | -138.98 | 17,424 |
| Ethylbenzene | 277.14 | -138.96 | 17,596 |
| 1,2-Dimethylbenzene | 291.95 | -13.32 | 17,547 |
| 1,3-Dimethylbenzene | 282.38 | -54.17 | 17,543 |
| 1,4-Dimethylbenzene | 281.03 | +55.87 | 17,547 |
| n-Propylbenzene | 318.59 | -147.10 | 17,722 |
| Isopropylbenzene | 306.31 | -140.85 | 17,712 |
| 1-Methyl-2-ethylbenzene | 329.27 | -113.50 | 17,693 |
| 1-Methyl-3-ethylbenzene | 322.34 | -139.99 | 17,685 |
| 1-Methyl-4-ethylbenzene | 323.57 | -80.23 | 17,681 |
| 1,2,3-Trimethylbenzene | 348.94 | -13.68 | 17,650 |
| 1,2,4-Trimethylbenzene | 336.82 | -46.84 | 17,638 |
| 1,3,5-Trimethylbenzene | 328.48 | -48.50 | 17,632 |
| n-Butylbenzene | 361.88 | -126.35 | ----- |
| Isobutylbenzene | 342.96 | -60.66 | ----- |
| sec-Butylbenzene | 343.94 | -103.85 | ----- |
| tert-Butylbenzene | 336.40 | -72.13 | ----- |
| 1-Methyl-4-isopropylbenzene | 350.78 | -90.4 | ----- |
| 1,2-Diethylbenzene | 362.26 | -24.5 | ----- |
| 1,3-Diethylbenzene | 358.03 | -119.06 | ----- |
| 1,4-Diethylbenzene | 362.80 | -45.8 | ----- |
| 1,3-Dimethyl-5-ethylbenzene | 362.75 | -119.6 | ----- |
| 1-Methyl-3-tert-butylbenzene | ^b 372.61 | ^b -42.76 | ----- |
| 1-Methyl-4-tert-butylbenzene | ^b 378.72 | ^b -62.92 | ----- |
| 1-Methyl-3,5-diethylbenzene | ^b 393.01 | ^b -101.21 | ----- |
| 1,3,5-Triethylbenzene | ^b 420.35 | ^b -87.59 | ----- |

^aAmerican Petroleum Institute Research Project 44.^bNational Advisory Committee for Aeronautics.

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TABLE III - F-3 AND F-4 PERFORMANCE NUMBERS OF ETHER BLENDS^a

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| Ether | Formula | F-3 | | | | F-4 (F/A=0.11) | | | | | |
|---|-----------------------------------|---|-----|---|-----|---|-----|-----|-----|-----|-----|
| | | Unleaded | | 4ml TEL/gal | | Volume-percent ether in blend with mixed base fuel ^b | | | | | |
| | | Volume percent ether in blend with S reference fuel | | Volume percent ether in blend with S reference fuel | | 4ml TEL/gal | | | | | |
| | | 10 | 20 | 10 | 20 | 10 | 25 | 50 | 10 | 25 | 50 |
| Methyl <u>tert</u> -butyl ether | C ₅ H ₁₂ O | 100 | 102 | 149 | 153 | 134 | 143 | 150 | 137 | 175 | 250 |
| Ethyl <u>tert</u> -butyl ether | C ₆ H ₁₄ O | 100 | 104 | 157 | 161 | 140 | 144 | 150 | 132 | 150 | 185 |
| Isopropyl <u>tert</u> -butyl ether | C ₇ H ₁₆ O | 103 | 104 | 160 | 161 | 137 | 149 | 160 | 126 | 150 | 185 |
| Methyl phenyl ether (anisole) | C ₇ H ₈ O | 93 | 90 | 141 | 121 | 118 | 107 | 94 | 125 | 142 | 137 |
| Ethyl phenyl ether (phenetole) | C ₈ H ₁₀ O | 99 | 97 | 140 | 120 | 120 | 111 | 100 | 128 | 146 | 137 |
| Methyl <u>p</u> -tolyl ether (<u>p</u> -methylanisole) | C ₈ H ₁₀ O | 99 | 99 | 144 | 133 | 120 | 112 | 100 | 133 | 145 | 136 |
| <u>m</u> -Methylanisole | C ₈ H ₁₀ O | --- | --- | --- | --- | --- | 110 | --- | --- | 147 | --- |
| <u>o</u> -Methylanisole | C ₈ H ₁₀ O | --- | --- | --- | --- | --- | 82 | --- | --- | 94 | --- |
| <u>p</u> - <u>tert</u> -Butylanisole | C ₁₁ H ₁₆ O | --- | --- | --- | --- | --- | 110 | --- | --- | 147 | --- |
| <u>n</u> -Propyl phenyl ether | C ₉ H ₁₂ O | --- | --- | --- | --- | --- | 110 | --- | --- | 149 | --- |
| Isopropyl phenyl ether | C ₉ H ₁₂ O | --- | --- | --- | --- | --- | 110 | --- | --- | 150 | --- |
| <u>tert</u> -Butyl phenyl ether | C ₁₀ H ₁₄ O | --- | --- | --- | --- | --- | 107 | --- | --- | 137 | --- |
| Methyl benzyl ether | C ₈ H ₁₀ O | --- | --- | --- | --- | --- | 104 | --- | --- | 111 | --- |
| Isopropyl benzyl ether | C ₁₀ H ₁₄ O | --- | --- | --- | --- | --- | 119 | --- | --- | 140 | --- |
| Phenyl methallyl ether | C ₁₀ H ₁₂ O | --- | --- | --- | --- | --- | 48 | --- | --- | 64 | --- |
| Methyl methallyl ether | C ₅ H ₁₀ O | --- | --- | --- | --- | --- | 93 | --- | --- | 92 | --- |
| Isopropyl methallyl ether | C ₇ H ₁₄ O | --- | --- | --- | --- | --- | 106 | --- | --- | 102 | --- |
| <u>tert</u> -Butyl methallyl ether | C ₈ H ₁₆ O | --- | --- | --- | --- | --- | 106 | --- | --- | 109 | --- |
| Dimethallyl ether | C ₈ H ₁₄ O | --- | --- | --- | --- | --- | 77 | --- | --- | 90 | --- |
| Methyl cyclopropyl ether | C ₄ H ₈ O | --- | --- | --- | --- | --- | 76 | --- | --- | 94 | --- |
| Methyl cyclopentyl ether | C ₆ H ₁₂ O | --- | --- | --- | --- | --- | 80 | --- | --- | 83 | --- |
| Methyl cyclohexyl ether | C ₇ H ₁₄ O | --- | --- | --- | --- | --- | 68 | --- | --- | 79 | --- |
| Propylene oxide | C ₃ H ₆ O | --- | --- | --- | --- | --- | 100 | --- | --- | 131 | --- |

^aPerformance numbers greater than 161 were determined as follows:

$$\text{Performance number} = \frac{\text{imep of blend}}{\text{imep of S+6 ml TEL/gal}} \times 161$$

^bThe mixed base fuel contained 87.5 percent (by volume) S reference fuel and 12.5 percent n-heptane. This blend was leaded to .4 ml tetraethyl lead per gallon and had F-3 and F-4 performance numbers of 120 and 112, respectively.^cApproximate value

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TABLE IV - PHYSICAL PROPERTIES OF ETHERS^a

| Ether | Boiling point (°F) | Freezing point (°F) |
|---------------------------------------|-----------------------|------------------------|
| Methyl tert-butyl ether | 131.18 | -163.57 |
| Ethyl tert-butyl ether | 162.86 | -137.20 |
| Isopropyl tert-butyl ether | 189.68 | -126.53 |
| Diisopropyl ether (literature value) | 155 | -76 |
| Methyl phenyl ether (anisole) | 308.48 | -34.80 |
| Ethyl phenyl ether (phenetole) | 337.82 | -21.05 |
| Methyl p-toly ether (p-methylanisole) | 350.06 | -25.69 |
| m-Methylanisole | 349.70 | -68.66 |
| o-Methylanisole | 341.24 | -29.38 |
| p-tert-Butylanisole | 433.76 | +66.45 |
| n-Propyl phenyl ether | 372.74 | -16.76 |
| Isopropyl phenyl ether | 350.24 | -27.49 |
| tert-Butyl phenyl ether | ^b 143.24 | -.958 |
| Methyl benzyl ether | 338.90 | -62.73 |
| Isopropyl benzyl ether | ^c 181.40 | -88.94 |
| Phenyl methallyl ether | ^d 175.28 | -27.96 |
| Methyl methallyl ether | 151.16 | -171.56 |
| Isopropyl methallyl ether | 218.98 | ----- |
| tert-Butyl methallyl ether | 248.92 | -120.30 |
| Dimethallyl ether | 273.88 | -71.72 |
| Methyl cyclopropyl ether | 112.51 | -182.34 |
| Methyl cyclopentyl ether | 221.79 | -210.75 |
| Methyl cyclohexyl ether | 272.12 | -101.87 |

^aNational Advisory Committee for Aeronautics^bAt 10 mm^cAt 16 mm^dAt 8 mm

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AROMATIC AMINES IN AVIATION GASOLINE

INTRODUCTION

Aniline and its derivatives have been recognized as antiknock agents for at least thirty years. During World War II they were given serious consideration as additives for aviation fuels. Methyl aniline received particular attention in Great Britain, and a xylidine mixture was manufactured for this purpose in the United States. Lack of materials and manufacturing capacity prevented wide use in Great Britain, and its use in this country was modest because the necessary fuel volume was acquired in other ways.

The possible desire to reduce the lead content of Grade 115/145 without affecting the rich mixture performance rating and the lack of availability of aromatics to accomplish this have emphasized the necessity for a review of the information available on the suitability and availability of aromatic amines as additives in aviation gasoline. It is the purpose of this appendix to review the available information on aromatic amines and set forth the advantages and disadvantages of using aromatic amines.

DISCUSSION

Antiknock Effectiveness

Normally processed alkylate is the most economical component for the production of fuels having performance numbers in excess of Grade 100/130. Unfortunately, a fuel largely composed of normally processed alkylate and not containing aromatics will have a rich/lean performance number ratio which is close to 1.1 and thus, in the case of Grade 115/145, the lean rating has to be considerably exceeded in order to meet the rich requirement. Aromatic amines are an attractive answer to this problem, since they are substantially without effect upon lean ratings and they significantly improve rich ratings. However, in engines which are milder than the F-3, aromatic amines may become very effective lean mixture antiknocks when used in conjunction with lead. If engines are mild at lean mixture, then the use of aromatic amines promises considerable increase in lean performance number. This increase would be obtained without the colossal steel requirements necessary to increase performance number by means of sensitive paraffins such as diisopropyl.

As antiknock agents, aromatic amines are 3.5 to 5 times as effective as aromatics but only about 1/10 as effective as tetraethyl lead. Accordingly the customary amine concentration in aviation gasoline is from 0.5% to 3.0%. With the exception of CS no very

extensive correlations of the variation in rich mixture effectiveness of amines with concentration and rating level have been established. It is possible, however, largely on the basis of data obtained by the NACA to predict the effectiveness of other aromatic amines relative to CS upon which more extensive correlations have been established.

During World War II considerable information was obtained on the effect of CS on octane number ratings. Several hundred ratings were obtained by a large number of laboratories on its effectiveness in the range of 100 to 130 performance number base stock. These data were collected by the Aviation Gasoline Advisory Committee, Subcommittee on Blending Octane Numbers and are reported in detail in Report No. 5 of that Subcommittee dated June 1, 1944. Figure 1 shows the effect of CS concentration on the F-4 rating of aviation fuels. Data on blending CS into very low or very high quality stocks are limited and the correlation of Figure 1 in these ranges should be accepted only as an indication. It will be noted that the blending index number of CS varies with both the concentration of CS in the blend and with the octane number level of the base stock. In Grade 130 fuel CS has a blending index number of approximately 1100 and in Grade 145 approximately 900 when used in a 1% concentration.

The AGAC Subcommittee indicates that available data on the F-3 blending value of CS are too scattered to permit development of a firm correlation. They recommended that 100 octane number be used as the F-3 blending value of CS with 4.0 ml TEL per gallon in all computations involving CS blending. This value was found to be quite satisfactory in all blending calculations that were made subsequent to the issuance of their report during quite extensive use of CS during the past war.

The AGAC Subcommittee points out that the bulk of the CS blending values were obtained in gasolines containing 4.0 ml TEL per gallon. No reliable data were available at the time to indicate the effect of TEL content on the F-3 and F-4 blending values of CS. Subsequent experience indicated that the blending values of CS were substantially the same in the presence of 4.6 ml TEL per gallon.

The NACA has in the past accumulated considerable data on the antiknock characteristics of aromatic amines using laboratory engines. Table I is a summary of the performance of forty-three aromatic amines evaluated in the F-3 engine at standard conditions and in the F-4 engine at three sets of conditions including the standard. The three sets of conditions used in the F-4 engine are:

| | F-4 | A | B |
|---------------------------|------|------|------|
| Engine speed, rpm | 1800 | 1800 | 1800 |
| Compression ratio | 7.0 | 7.0 | 7.0 |
| Inlet-air temperature, °F | 225 | 250 | 150 |
| Spark advance, °BTC | 45 | 30 | 30 |
| Coolant temperature, °F | 375 | 250 | 250 |

The F-4 conditions are considered the most severe and the B conditions the mildest. Condition A is intermediate in severity between these two. Although it is difficult to draw any systematic relationship between structure and antiknock effectiveness from this table, it seems evident from these data that:

1. Monomethyl amines are generally more effective than the parent amines.
2. Monomethyl substitution is optimum, being more desirable than either monoethyl or dimethyl substitutions.
3. The para structure is far superior to the ortho structure.
4. The monomethyl derivatives of aniline and toluidine should be given first consideration as antiknock additives.

The NACA data on xylidines agree within experimental error with the correlation established by the AGAC Subcommittee on Blending Octane Numbers. On the basis of all of the available laboratory knock test data, both monomethyl aniline and monomethyl toluidine appear to be 1.2 times as effective as CS. Mixed toluidines, on the other hand, appear to be quite similar to CS in effectiveness. These appear to be the only four materials that deserve consideration from the availability and effectiveness standpoints.

The evidence obtained during World War II would indicate that the gains in rich performance due to the addition of aromatic amines were also shown in full-scale engines. That fuels containing aromatic amines may show knock limited performance in mild engines which is greatly in excess of what would be predicted by lean and rich ratings is seen by considering data obtained by the Packard Motor Car Company on a Packard Rolls-Royce Merlin with two-stage supercharger and after-cooler (which enabled mixture temperature to be controlled) at 3000 RPM. The knock limited indicated power obtained at 140°F mixture temperature and 0.073 F/A was 20 percent higher on Grade 100/150 containing 3 volume per cent xylidines than it was on Grade 100/130 containing no amines. At 275°F mixture temperature and 0.10 fuel-air ratio Grade 100/150 permitted 27 percent more power than Grade 100/130. At 275°F mixture temperature and 0.076 fuel-air ratio Grade 100/150 permitted 29 percent more power than Grade 100/130. The fact that contrary to expectations Grade 100/150 permitted a greater power increase at the higher mixture temperature was almost certainly due to improved distribution at the higher temperature. These data were chosen from a large amount of available full-scale data since they best illustrate the fact that aromatic amines may be more effective than the F-4 method would suggest and, furthermore, that they are highly effective lean mixture antiknocks in mild full-scale engines.

Although no actual data were obtained in full-scale equipment there is reason to believe that aromatics themselves would have shown the same gains in rich mixture performance ratings over those indicated by results obtained by the F-4 method. Further, there is little question that the aromatics would be far more effective under lean mixture conditions in mild full-scale engines than would be indicated by ratings obtained using the F-3 method.

Full-scale single-cylinder engine knock tests made at the NACA indicate that of the two aromatic amines which have been considered previously as additives, monomethyl aniline and mixed xylidines, the former is somewhat more effective than the latter at both lean and rich mixtures. This can be easily seen in the following table which is a comparison of the antiknock effectiveness of several aromatic amines tested in 28-R fuel with the Wright R-1820 G-200 single cylinder.

Ratio of the IMEP of 98 percent 28-R plus
2 percent by weight aromatic amine
to the IMEP of 28-R

| | <u>.07 F/A</u> | <u>.10 F/A</u> |
|---|----------------|----------------|
| 28-R Fuel | 1.00 | 1.00 |
| N methyl xylidine (mixed isomers) | 1.25 | 1.12 |
| N methyl toluidines (75 percent <u>p</u> 25 percent <u>o</u>) | 1.39 | 1.14 |
| Xylidines (mixed isomers) | 1.24 | 1.11 |
| N methyl aniline | 1.36 | 1.15 |

This table also shows the effectiveness of N methyl toluidines, especially at lean mixtures. It is also seen that the methyl xylidines are only very little better than the mixed xylidines as indicated by the small-scale data.

CS and MMA were used in modest amounts during the past war by both the United States and British Air Forces. CS was used in approximately 1% concentration with either 4.0 or 4.6 ml TEL per gallon in Grades 98/130 and 99/130 aviation fuels under specifications AN-F-27 and AN-F-27a. The former specification was in effect from July 10, 1943 until June 1944 and the latter from this point until the end of the war. Grade 93/110 containing 3% CS and 6.0 ml TEL per gallon was given some consideration for use as a substitute in training operations within the continental United States during 1944. After limited experimental flight testing this fuel was found not to be acceptable because of engine operating difficulties.

CS was also used to a minor extent in the production of 100/150 aviation fuel, a specification originally drawn by the British in January 1944. This specification level was attained by using a lead content of 6.0 ml per gallon and by using 2.5% monomethyl aniline or 3% CS. Only a very small amount of CS was ever used inasmuch as capacity in England to produce monomethyl aniline was sufficient to fulfill requirements.

In all cases in the use of these fuels the antiknock effectiveness displayed by CS or monomethyl aniline in the F-3 and F-4 engines was either equaled or exceeded in full-scale engine operation.

General Suitability of Aromatic Amines

Volatility Characteristics. All aromatic amines boil above the AN-F-48a end point specification (338°F) and therefore can logically be considered as high-boiling fuel contaminants. The Esso Laboratories have made a study of the effect of xylidines (boiling at 420°F) on aviation gasoline volatility and have found a correlation between xylidine concentration and change in the ASTM 50 percent, 90 percent and end point temperatures. It was found that for each one percent addition of xylidine, the ASTM 50 percent temperature increases by 1-1/4°F, the 90 percent temperature increases by 7-1/2°F, and the end point increases by approximately 20°F. It can be seen that xylidines exert the largest effect on ASTM Final Boiling Point; however, the effect is partially dependent upon the final boiling point of the aviation gasoline. Although the ASTM 90 percent point of xylidine is roughly 420°F, experience during the last war indicated that a final boiling point requirement of 374°F on the total fuel was not exceeded.

There are indications that the increase in final boiling point with the addition of xylidine exerts a deleterious effect on lead fouling susceptibility. Service records indicate that when a concentration of 6.0 ml TEL per gallon was used in conjunction with xylidine and monomethyl aniline marked increase in engine failures on takeoff occurred, particularly with liquid cooled engines. Recent studies by Professor G. G. Lamb, Northwestern University, would indicate that the fouling problem may be aggravated by the high boiling components not vaporized completely during the combustion process. It is suggested that droplets of this higher boiling point component probably form a nucleus in which part of the TEL remains in liquid form and therefore is ineffective. Since the aromatic amines which can logically be considered from an availability and antiknock standpoint all boil from 380°F to 425°F, there is little to choose between these compounds from a volatility standpoint.

Solubility in Gasoline. Aniline is practically insoluble in paraffins at temperatures below 0°F, but the addition of alkyl

groups increases its solubility. This is especially true if the alkyl group is attached to the nitrogen; 2 percent of N methyl aniline will dissolve in a paraffinic fuel at -76 F. Insertion of alkyl groups in the ring is much less effective. Solubility is moreover roughly inversely proportional to freezing point, so that ring-substituted para-toluidine and 4-amino-ortho-xylene, which have freezing points far above aniline, are just about as insoluble. A comparison of the gasoline solubility at -76°F of the three aromatic amines most commonly considered from an availability standpoint can be seen by an inspection of the following table, wherein the percent by weight of amine which can be added to three representative gasolines is listed.

| | Aromatic-free 65 O.N. gasoline | 65 O.N. gasoline +15% aromatic | AN-F-28 |
|--|-----------------------------------|-----------------------------------|---------|
| N methyl toluidines (75 percent <u>p</u> 25 percent <u>o</u>) | > 10 | > 10 | > 10 |
| Mixed xylidines | 3.7 | > 10 | > 10 |
| N methyl aniline | 3.6 | 12 (-80°F) | > 10 |

The fuel solvent has its expected effect; amines are far more soluble in aromatics than in saturates, and considerably more soluble in naphthenes than in paraffins.

Toxicity. Amines are toxic materials. CS, MMA and the toluidines have been manufactured and used industrially in comparatively small quantities for a long time and possess fairly well defined toxic properties. As close relatives of the aniline group, it would be expected that the most severe effects would be methemoglobinemia and cyanosis. It is against these two types of intoxication that manufacturers have always instituted safeguards. During the last war when it appeared likely that mixed xylidines would be used in relatively large quantities as an additive to aviation fuels, it was realized that a considerable number of individuals might experience potential exposure and that, therefore, the hygienic aspects of the problem should be made the subject of additional research by qualified industrial toxicologists. Such studies were undertaken by the Division of Industrial Hygiene of the U. S. Public Health Service and by the Kettering Laboratory of Applied Physiology. Problems involving the manufacture, transportation, handling of the raw material in the form of nitroxylenes, storage and blending were considered. Complete results of the studies are available in the files of the U. S. Public Health Service.

The aromatic amines can be absorbed into the human system in identically the same way as tetraethyl lead although the physical effects are entirely dissimilar. Since this was the case, the recommended method of handling CS during the last war was similar to that of handling tetraethyl lead. Steps were taken to conduct

the material in entirely closed systems throughout storage and transfer. Transportation of the finished product from the manufacturing locations to the blending locations was in all cases by means of tank cars having only top unloading connections to avoid spills.

The research programs indicated that little or no trouble from the hygienic point of view would be expected from the handling of finished fuel containing concentrations of 3% CS or less. It was further recognized that all gasoline containing CS would also contain tetraethyl lead and that, for this reason, the extremely exacting precautions used in cleaning tanks which had contained leaded fuels would suffice also for tanks which had been used in the storage of fuels containing both CS and tetraethyl lead.

The two research organizations investigating the toxicological effects of CS stated that while it produced a somewhat less severe aniline effect than might have been expected, it would have a serious effect upon the liver and, for that reason, uncontrolled exposure might well have been extremely unfortunate. It is significant that relatively large quantities of CS were handled during the life of the program during the last war and no case of CS poisoning was reported. It seems logical to conclude, therefore, that the handling problems of amines are not unsurmountable since the toxicological effects of those suitable for aviation fuel blending should be similar to those of CS and, under any circumstances, not more severe than those encountered with aniline.

Stability. Fuels containing aromatic amines tend to be more unstable than the base fuel into which they are blended. This matter was very carefully studied in connection with the use of CS. This material is subject to oxidation by contact with air and to subsequent discoloration. This factor caused no extensive difficulty in itself since the addition of minute quantities of an approved aviation gasoline oxidation inhibitor and careful handling including storage under a blanket of inert gas maintained proper color between the time of manufacture and the time of blending.

Storage tests of CS blends were undertaken under the auspices of the Coordinating Research Council, CFR-AFD Gasoline Additives Advisory Group. Reports have been issued under the title "1944 Desert Storage Tests on Aviation Gasoline With and Without CS." It was apparent that CS led very substantially to instability and only a small portion of the samples tested was satisfactory beyond 12 months storage under desert conditions. The severity of the storage conditions in these tests should be considered in weighing the results obtained.

Over-Water Storage. Water solubility of an aviation fuel component is important since stored gasoline is nearly always in contact with water. The distribution coefficient of CS is generally found

to be in the range of 12 to 18 at 60°F. This figure decreases with temperature and aromaticity of the fuel into which CS is blended and decreases with lowered pH values of the water. In ordinary storage systems, when the quantity of water is not large, the loss of CS is not very significant.

However, the Services use quite extensively the so-called "aqua system" for working storage. This system involves displacement of the fuel in the storage system by water as the gasoline is used. A somewhat similar system is used on aircraft carriers but here conditions are more favorable for water extraction of water soluble material in the gasoline because of more or less constant motion of the ship and resulting changes in interfacial layers of water and gasoline. Service tests aboard an aircraft carrier revealed that over a period of two weeks with two water changes the CS content of the fuel decreased by 20% with a corresponding loss of 10 performance numbers in rich mixture rating.

Limited data would indicate that the distribution coefficients for monomethyl toluidine, toluidine and monomethyl aniline would be lower and would decrease in that order.

Solvency Characteristics. Aromatic amines have five to ten times the solvent effect of aromatic hydrocarbons found in aviation gasoline. Their use, therefore, would increase the fuel's tendency to attack rubber and synthetic materials in the aircraft fuel system and also in ground fuel dispensing systems. This solvency characteristic caused rather widespread difficulty in aircraft equipment during the last war, especially when CS or MMA was used in 3% concentrations. Trouble was experienced in varying degrees of severity with tank liner patching material and other synthetic or rubber substitute materials in accessories such as selector valves and carburetor diaphragms in the fuel induction system. Improvements made during the last war and subsequent improvements in the solvent resistant characteristics of synthetics reduces the possibility of difficulty with present-day aircraft.

Freezing Point. Aromatic amines have freezing points substantially higher than aviation fuel. However, mixed xylidines, methyl toluidines, toluidines and monomethyl aniline can be used in concentrations up to 3% without significant difficulty in meeting the currently specified freezing point of -76°F. While such fuels meet the laboratory freezing point specification, it is open to question as to whether the fuels may not show a greater filter clogging tendency than will straight hydrocarbon fuel.

General Engine Performance. General engine performance data are available only on aviation gasoline blends containing xylidines and monomethyl aniline. Although nearly 11,500,000 barrels of Grade 98/130 containing 1% CS and over 7,000,000 barrels of Grade 99/130 containing 1% CS were used during the last war there are but few official reports giving actual flight experience with CS fuels.

Grade 100/150 which was used in England by both British and American Air Forces contained 6.0 ml TEL per gallon and either 2.5% MMA or 3% CS. By far a larger portion of the fuel was blended with MMA. No accurate records are available on the production of this type of fuel although it is believed that at times it amounted to as much as 10 to 12 thousand barrels per day. It is reported that it found extensive use in interceptor aircraft and was also used in Army Air Forces equipment accompanying bombers on long-range missions over Germany.

Some records are available which indicate that difficulties were encountered that could be related to the physical and chemical characteristics of the amines. These were appreciably more numerous in fuels that contained 3% CS and 6.0 ml TEL per gallon. It was generally conceded that fuels containing amines were adversely affected similar to any fuel with a high aromatic content by high mixture temperatures such as those encountered in long-range cruising operations in bomber escort missions. Under these conditions excessive spark plug gap wear and fouling were reported. There was some evidence although not conclusive that amines, particularly CS, contributed to carburetor fouling, piston ring scuffing and sticking and piston head burning.

More precise records were kept on Service tests conducted on Grade 93/110 containing 3% CS and 6.0 ml TEL per gallon. Increased valve and piston deposits were found here, a condition to which the added amount of tetraethyl lead undoubtedly also contributed. Service and maintenance records seem to indicate that aircraft engines and accessories manufactured for the Royal Air Forces were less susceptible to the deleterious effects of amino aromatics. It is understood that numerous changes were made in American aircraft at British bases utilizing this fuel so that, according to some reports, it caused no more mechanical troubles or servicing difficulties than did Grade 100/130.

The increased depositing tendencies occurring with the use of aromatic amines can probably be attributed in part to their volatility. The deposits are of the varnish and sludge type rather than the type produced by tetraethyl lead. The NACA has investigated the effect of low carburetor air temperature upon engine operation with a fuel containing about 3% of high boiling component and found appreciable evidence of increased amounts of incompletely burned fuel residue transferred to the lubricating oil by the blow-by fuel gases passing the piston rings.

The tendency of an engine utilizing fuel containing aromatic amines to have ring sticking troubles seems definitely to increase altogether apart from any ring sticking effect resulting from increased permissible power output. There is some evidence, however, to indicate that with regard to sludge and ring sticking concentrations of aromatic amines up to 2% can be tolerated.

Addition of aromatic amines to any given fuel increases the tendency to preignition. This was a significant difficulty with the Rolls-Royce Merlin in British service using Grade 100/150 fuel. Substantially, however, difficulty with preignition is the result of increased fuel sensitivity and other components producing equal sensitivity would produce in general similar reductions in resistance to preignition tendency.

There appear to be no contrary indications whatsoever to the statement that aromatic amines do contribute markedly to improved performance in full scale engines in service when operating under rich fuel-air mixture conditions.

Potential Availability of Aromatic Amines

The foregoing discussion has indicated that mixed toluidines, mixed xylidines, and monomethyl derivatives of aniline, toluidine, and xylidines (CS) do possess known valuable properties as aviation fuel additives. This section will discuss the manufacturing aspects of these materials and present estimates of the basic raw material needs associated with the manufacture of large amounts for extensive use in military aviation gasolines.

Preferred Processes. The normal method for making primary aromatic amines (e.g., aniline, toluidine, xylidines) involves nitration of the corresponding aromatic hydrocarbons followed by reduction to produce the amine. This method is currently used to produce aniline and was used in the last war to produce xylidines. An alternative method is to chlorinate the hydrocarbon and then treat the resultant product with ammonia. However, to produce 5,000 to 15,000 barrels per day of amine would require on the order of 200,000 to 700,000 tons of chlorine annually, or from one-sixth to one-half of the country's 1944 production. In view of the large use of electric power which chlorine manufacture entails and the fact that its production is tied to that of caustic soda, expansion of chlorine capacity would probably be quite difficult. On the other hand, it appears that nitric acid capacity could be readily expanded, and the nitration process is therefore considered more attractive. Hydrogenation capacity similar to that used for the manufacture of CS during the last war could be made available quite readily for the reduction of the nitro intermediates.

The manufacture of the monomethyl derivatives of the primary amines is at present carried out only on a quite small scale. To maintain the quality of the product as an aviation gasoline additive it would be essential to keep contamination by the dimethyl component to a minimum. Three processes appear to be potentially applicable. The first process involves the condensation of formaldehyde with the amine under hydrogenation conditions to produce an essentially pure mono substituted product. The second involves

condensation of methanol with the amine followed by separation and recycle of the disubstituted by-product to the reaction. The known chemical separation steps require a large use of chemicals. This latter procedure was used in England during the last war quite successfully. The third involves an improved process now indicated to be available which involves the catalytic methylation of the amine in the vapor phase. This procedure has not been developed beyond the pilot plant stage and would, therefore, require a more thorough evaluation. Pending this it does, however, appear to be the most attractive method of producing the monomethyl derivatives.

It should be pointed out that one of the advantages of xyliidines is the elimination of the methylation step in the production process.

Raw Material Requirements. Regardless of the process used in the manufacture of MMA, aniline is required as a raw material. This chemical is in turn, derived from benzene. The lack of availability of benzene under emergency conditions is, therefore, an important factor against planning on the use of MMA. It is conceivable, however, that should MMA appear to be far more attractive than other aromatic amines from the utilization standpoint, some benzene might be made available from the indicated supplies by substituting other aromatics and other materials for benzene now assumed to be allocated to other essential uses. Further, additional amounts of benzene might be made available, undoubtedly at a substantial cost above the normal market value, by the dehydrogenation of cyclohexane and methylcyclopentane obtained by the fractionation of selected gasoline stocks. Facilities for these operations would have to be constructed. Methanol, required in the methylation step, could undoubtedly be made available in the quantities required.

It can be assumed that at least 1.2 to 1.5 volumes of benzene would be required for each volume of MMA produced.

The basic raw materials required for mixed toluidines would be toluene, nitric acid, and hydrogen. No toluene would be available for aviation fuel purposes certainly during the early stages of emergency. Additional production facilities would have to be installed to obtain toluene either by extraction from certain catalytically cracked fuels or by a combined hydroforming and extraction operation. Nitric acid, hydrogen, and the facilities for the nitration and reduction steps are available to a degree and could undoubtedly be expanded rapidly.

It can be assumed that approximately 1.4 volumes of toluene would be required to produce one volume of mixed toluidines.

The basic raw materials required for monomethyl toluidine would be toluene, nitric acid, hydrogen and methanol. Approximately 1.4 volumes of toluene would be required for the toluidine intermediate

and since the methylation step is not quantitative, toluene requirements would probably be somewhat higher than in the case of producing toluidine itself. Nitric acid, hydrogen, and methanol requirements could undoubtedly be met.

The basic raw materials required for the production of mixed xylidines would be xylene, nitric acid, and hydrogen. Among benzene, toluene, and xylene the latter would be most readily obtainable under emergency conditions. During the last war arrangements were made to provide approximately 2500 barrels per day as a by-product from toluene manufacture. This quantity could be readily supplemented by the addition of fractionation and extraction facilities to process catalytically cracked stocks that probably would not otherwise be required in the aviation gasoline program.

From the standpoint of overall raw material requirements and processing requirements, mixed xylidines (CS) could undoubtedly be most readily supplied in case of an emergency. The following table indicates the estimated basic raw material requirements for producing various aromatic amines at a 1000 barrel per day production rate:

Approximate Raw Material Requirements for Producing
1000 B/D of Various Aromatic Amines

Monomethyl aniline

| | |
|--------------------|------------------------------|
| Benzene | 1,400 B/D |
| Nitric Acid (100%) | 180 tons/D |
| Methanol | 18,000 gal/D |
| Hydrogen | 7 million ft ³ /D |

Toluidines

| | |
|--------------------|--------------------------------|
| Toluene | 1,420 B/D |
| Nitric Acid (100%) | 147.5 tons/D |
| Hydrogen | 5.3 million ft ³ /D |

Monomethyl Toluidines

| | |
|--------------------|------------------------------|
| Toluene | 1,500 B/D |
| Nitric Acid (100%) | 160 tons/D |
| Methanol | 18,000 gal/D |
| Hydrogen | 7 million ft ³ /D |

Xylidines

| | |
|--------------------|--------------------------------|
| Xylene | 1,400 B/D |
| Nitric Acid (100%) | 127 tons/D |
| Hydrogen | 4.6 million ft ³ /D |